Geophysical Research Abstracts
Vol. 15, EGU2013-2571, 2013
EGU General Assembly 2013

Sorption reactivity of mineral surfaces: the model-free conversion of humidity effect on organic vapor sorption to the organic sorbate effect on water-sorbent interactions

Mikhail Borisover
The Volcani Center, A.R.O., Soil, Water and Environmental Sciences, Bet Dagan, Israel (vwmichel@volcani.agri.gov.il)

Interaction of water with mineral surfaces is one of the key factors controlling their reactivity towards organic compounds in multiple physical and chemical processes, e.g., in sorption and catalysis. Specifically, water interactions with minerals (as well as with other naturally present sorbents) are of fundamental importance for distribution of organic compounds between different environmental phases. Therefore, it is of basic interest to learn about interrelations between organic sorbate – sorbent and water - sorbent interactions on a local scale, in a microenvironment specific for a given organic sorbate. The understanding of these interrelations can be approached by examining the effect of organic compounds on water – sorbent interactions. However, at environmentally relevant conditions associated with relatively low concentrations of organic compounds, it may be hardly possible to directly measure the effect of sorbed organic molecules on water sorption. This paper reports a thermodynamic approach in which the effect of organic compounds on sorbent-water interactions can be obtained, in a model-free way, from the equilibrium sorption isotherms of organic vapors on a variously hydrated surface (Borisover, M., Adsorption, DOI 10.1007/s10450-012-9446-7). The outcome of this conversion is a "differential" stoichiometry between changes in the amounts of water and organic compounds in the sorbed state. The analysis included the experimental sorption data for various organic vapors on such environmentally important sorbents as quartz, metal oxides, calcite, clay minerals and humic acid. So, based on sorption isotherms of organic compounds obtained at different relative air humidities, the number of water molecules expelled from a sorbent or co-sorbed, per an organic molecule sorbed, may easily be obtained for any humidity range. This "differential" stoichiometry was also examined by means of the Linear Free Energy Relationship (LFER). Based on the LFER analysis, the role of volume of organic compounds, their hydrogen-bonding acidity and basicity and electronic polarizability in expelling water from inorganic surfaces was elucidated. The response of water - mineral surface interactions to the organic compound sorption differs from the response of water – organic (humic) matter interactions: the latter may become enhanced upon sorption of organic sorbates (such as containing oxygen, nitrogen or sulfur atoms). The described evaluation of the effect of sorbed organic compounds on sorbent-associated water and the further LFER analysis of this effect can be carried out on multiple types of surfaces which can be characterized by equilibrium sorption isotherms of water and organic vapors.